RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Photoemission studies of the high-T_c superconductor $Ba_2YCu_3O_{9-\delta}$

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(Received 8 April 1987)

Valence-band photoemission measurements have been made both above and below the T_c of $Ba_2YCu_3O_{9-\delta}$, where $\delta=2.1$. We find similarities to recent calculations of the electronic properties. However, the experimental binding energies are between 1.0 and 1.4 eV further from the Fermi level than the calculation. We suggest that this difference may affect attempts to predict T_c from tight-binding modeling of the electron-phonon mechanism.

The recent demonstration of high-temperature ($T_c \sim 30$ K) superconductivity in the Ba-La-Cu-O system by Bednorz and Müller[1] has led to an explosive growth of research activity into the superconducting properties of similar oxides.[2] In a very short time it has been demonstrated that even higher T_c's ($T_c=93$ K) can be achieved in the Y-Ba-Cu-O systems.[3] Subsequently it has been established that it is possible to isolate as a single phase high-T_c superconducting compound the oxygen-deficient perovskite of stoichiometry $Ba_2YCu_3O_{9-\delta}$.[4]

In parallel with these experimental demonstrations has been the publication of a number of theoretical papers describing the properties of these materials.[2] In particular, several band structures[5-7] have appeared and possible similarities between these oxides and the superconducting oxide $BaPb_{1-x}Bi_xO_3$ have been suggested.[5] Both the present oxides and the earlier lead bismate are found to be unique in having substantial O $2p$ character at the Fermi surface. It is suggested that these oxygen orbitals form strong bonds to the neighboring Cu or Pb/Bi atoms and that modulation of these bonds by breathing-type oxygen vibrations could lead to strong electron-phonon coupling and hence a higher T_c for these materials. On the other hand, several authors[8] have suggested alternative mechanisms to explain the high T_c's and certainly the outstanding theoretical problem in this field is the nature of the interaction that causes superconductivity in these materials.

Theoretical modeling of the electron-phonon interaction[9] is reliant on a tight-binding fit of the linearized augmented plane-wave band-structure calculations. It would, therefore, be of considerable interest to establish some experimental verification of the results of the band-structure calculations. Unfortunately, both the complexity of the valence-band structure and the fact that currently it is not possible to produce large single crystals of these materials limits photoemission studies to density-of-states measurements. In this paper we demonstrate that useful information regarding the densities of states may be obtained by comparing photoemission spectra for different incident photon energies. We are able to identify both the main copper components and the oxygen components in the density of states for the $Ba_2YCu_3O_7$ system. Our principal result is that while the copper and oxygen components have a similar energy separation to the calculation, both are shifted to higher binding energy with respect to the Fermi level by approximately 1.0 eV.

The experiments reported here have been carried out on two different photoemission systems. Both experimental chambers allowed the sample to be cooled significantly below T_c (~ 98 K for the present materials) and both systems employed hemispherical analyzers[10] for the energy analysis of the photoemitted electrons. In one system the photons (21.2 eV) were provided by a He resonance lamp (sample 1) and in the other apparatus photons were produced by the U5 uv undulator stationed on the National Synchrotron Light Source uv storage ring[11] (sample 2). We wish to emphasize that the samples used in the two chambers were of the same compound but from different sources.[12] These superconducting materials were manufactured using what are now well established techniques[4] and we show in Fig. 1 the resistance measurement as a function of temperature for sample 1. In both systems the material was cleaned by scraping the surface. In an unbaked chamber contamination of the samples quickly occurred and thus the results reported in this paper were all taken under UHV conditions. However, we note that baking ($\lesssim 100$ °C) the experimental chamber may have caused some loss of oxygen, an effect which is known to degrade the materials.

In Fig. 2 we compare the photoemission spectra recorded from sample 2 at photon energies of 45, 52, and 105 eV. These energies correspond to regions of the first and second harmonics of the undulator.[11] Also shown in Fig. 2 are photoemission spectra recorded from sample 1 at

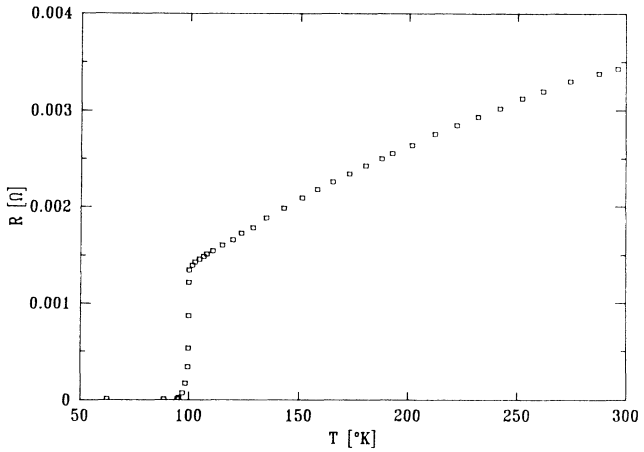

FIG. 1. Resistance in ohms as a function of temperature for sample 1. At 150 K the resistivity $\rho \sim 670\ \mu\Omega$ cm.

photon energies of 21.2 and 40.8 eV. On both samples it proved possible to identify the Fermi level. We show in the inset of Fig. 2 the Fermi level recorded from sample 1 at a photon energy of 21.2 eV. We would emphasize that this feature, which is a definite step, is approximately a factor of 50 smaller than the main peaks in the valence band. We also show in the inset the Fermi level following copper evaporation onto sample 1. The Fermi level recorded from this thin film, scaled to the same step height, confirms the Fermi level for the underlying superconducting material.

The spectra from sample 1 show two clearly resolved features at binding energies, determined through least-squares fitting to two Gaussians, of approximately 2.3 and 4.3 eV. At the slightly higher photon energy of 45.0 eV the spectrum from sample 2 still shows the 4.3- and 2.3-eV peaks although the 2.3-eV peak is slightly reduced relative to the 4.3-eV peak. At 52 eV the 2.3-eV peak is reduced still further and at 105 eV only the 4.3-eV peak is clearly resolved. Examination of photoionization cross-section tables[13] indicates that on going from 21.2 to 105 eV the cross section for photoionization of the O $2p$ level falls by over an order of magnitude. Over the same range there is very little change in the photoionization cross section of the Cu $3d$ levels. We, therefore, associate the peak at 4.3 eV with the copper density of states and the peak at 2.3 eV with the oxygen density of states. We note in passing that the Ba and Y are expected to contribute little to the density of states in the valence band.[7]

We note that all spectra in Fig. 2 were recorded immediately after scraping the sample. As a function of time it was noted that the intensity of the peak at 2.3 eV declined. We associate this decrease with oxygen leaving the freshly exposed surface. We also note the presence of a peak at a binding energy of 9.1 eV. This peak was observed on both samples prior to scraping or baking of the experimental chambers. Indeed, on both samples its intensity was initially comparable to that of the 4.3-eV binding-energy peak. After scraping under UHV conditions it had completely disappeared on sample 1 (21.2-eV spectrum) but was still observable on the photoemission

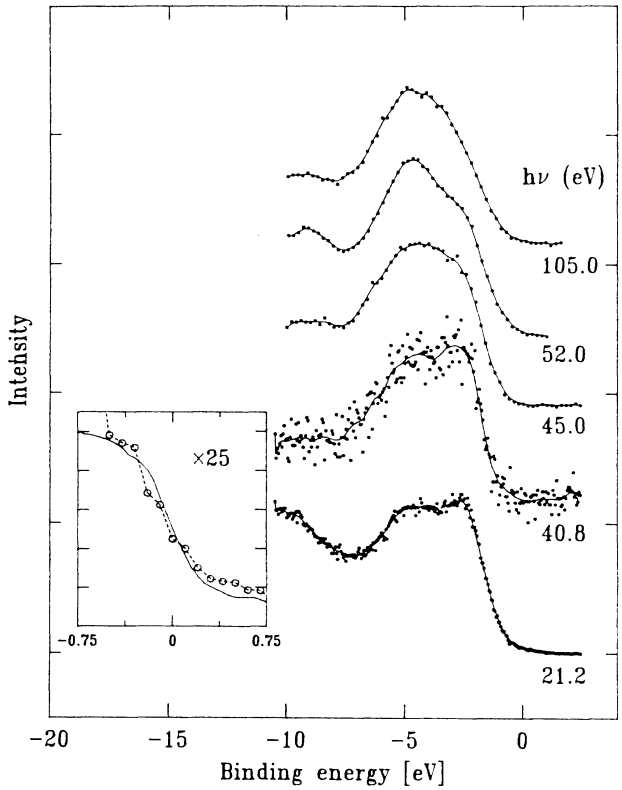

FIG. 2. Photoemission spectra at 45.0, 52.0, and 105.0 eV from sample 2. Photoemission spectra at 21.2 and 40.8 eV from sample 1. The inset shows the Fermi level step scaled by a factor of 25 from sample 1 at 21.2 eV (dashed line) and the Fermi level from a copper film (solid line) scaled to the same height.

spectra from sample 2. From its behavior as a function of photon energy we associate this peak with oxygen and suggest that it is characteristic of some other oxide produced during the annealing phase of the sample manufacture. As previously noted, in both systems it was possible to cool the sample below T_c. Essentially no change was observed in either the valence-band region or the Fermi energy region in going above or below T_c.

Thus we have identified the main oxygen and copper components in the density of states for the $Ba_2YCu_3O_7$ superconducting material. In Fig. 3 we compare the measured density of states at 21.2 eV with the calculated density of states. The experimental binding energies of these different components are 2.3 and 4.3 eV for oxygen and copper, respectively. The relative separation of 2.0 eV between these two components is less than the calculated separation of approximately 2.4 eV (Ref. 7) (Fig. 3) for the total density of states. We further note that both experimentally determined components are shifted to higher binding energies than the calculated muffin-tin projected densities of states[7] by 1.0 eV for the copper derived component and 1.4 eV for the oxygen component. We note that the higher binding energy shift on the oxygen component may reflect a loss of oxygen from the surface. The shifts could, of course, be characteristic of final-state relaxation or excited-state effects. However, in these metal-

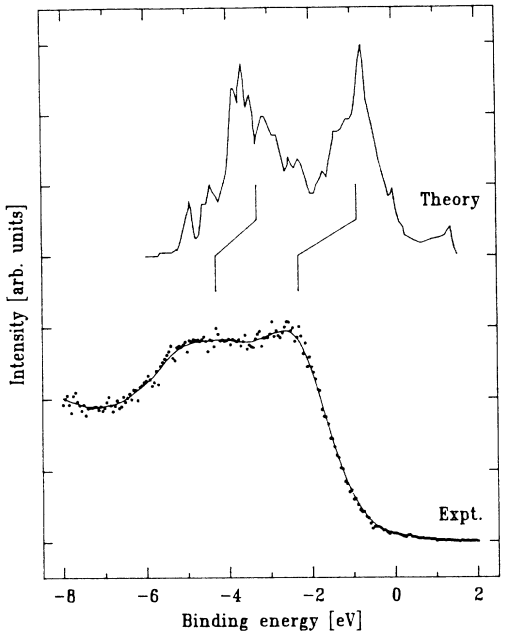

FIG. 3. Comparison of the 21.2-eV spectrum from sample 1 with the calculated density of states from Mattheiss and Hamann (Ref. 7).

lic systems, which display a two-dimensional electronic structure characteristic of their planar geometry, we would expect such effects to be small. Some of the shift may be accounted for through the accuracy of the local density approximation (LDA) in calculating the binding energy of localized d orbitals. It is well established that LDA tends to produce lower binding energies by approximately 1.0 eV for such orbitals as has previously been noted for copper.[14] Of course, these materials are complex and further discrepancy between theory and experiment may be introduced through a calculation based on an incorrect structure. Indeed, the structure used in the calculation is still undergoing refinement particularly with respect to the arrangement of oxygen atoms with respect to the central copper atom.[15] However, the layered nature of the materials suggests that such refinements would influence the projected density of states only on the central atoms. A final possibility that we consider is the presence of an oxygen deficiency which would tend to raise the Fermi level. While we note that this is indeed a possibility, we suggest that it is surprising that two samples from two different sources should produce identical densities of states. This would require the level of oxygen deficiency for the two samples to be nearly identical. However, we note again that such a deficiency could arise as a result of the scraping procedure.

In conclusion, we have measured the density of states for the superconducting compound $Ba_2YCu_3O_{9-\delta}$, where $\delta=2.1$. Our measured density of states is similar to the first-principles calculated density of states but there is an overall shift to higher binding energy. In particular, we note that a shift of the oxygen density of states with respect to the Fermi level has important implications for any tight-binding modeling of the electron-phonon interaction based on a first-principles LDA band-structure calculation. We propose that these deviations from the calculated band structure must be taken into account in any attempts to derive T_c using tight-binding modeling of the electron-phonon interaction for these materials.

We acknowledge useful discussions with J. W. Davenport, L. F. Mattheiss, and J. M. Tranquada. This work is supported by the Division of Materials Science, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

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